Spectromicroscopy of Mn Distributions in Micronodules produced by Bacterial Bio-mineralization

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INTRODUCTION

An understanding of the interaction of single cell microorganisms with inorganic substrates is a central issue in both aquatic and soil environmental chemistry. The biochemical pathways of bacterial metabolism based on redox reactions of transition metal compounds involve the processes of microbial attachment to and subsequent modification of inorganic surfaces, as well as the precipitation of inorganic compounds. Bacteria have been discovered which oxidize Mn or Fe into higher valence states, whereas others will reduce the oxides as part of their energy transport cycle [1,2]. Certain basic facts regarding the initial compounds formed by bacteria that metabolize Fe and Mn are still not fully understood. These issues are important to the understanding of bio-corrosion phenomena, to the microbial ecology of oxide precipitates formed by bacteria, and to the future harnessing of bio-mineralization for use in bio-remediation efforts and as a route to novel nanostructures.

This article is a report on the first results obtained for natural Mn nodules (from Green Bay sediment core samples) using high resolution soft x-ray spectromicroscopy at BL7. The first row transition metal L absorption edges, due to 2p→3d core transitions, expose a rich fine structure which allows to differentiate between several valence states of the metal ion. Without spatial resolution, these studies have been seriously limited, because the action of the microorganisms is not spatially homogeneous. This is clearly demonstrated by the comparison of the microspectroscopic measurements to spatially averaging total yield measurements.

EXPERIMENT

One of the major advantages of high resolution soft x-ray absorption spectroscopy at the scanning transmission microscope STXM (ALS *SpectroMicroscopyFacility*) is the possibility to investigate systems in their natural aqueous environments. Measurements on dried samples may not represent the natural state due to chemical or structural changes. For the investigations presented here, by placing the Mn specimens between two Si_3N membranes x-ray transparent wet-cells containing a thin water film have been performed. The adjustment of a thin layer of water by means of capillary forces has been improved by covering the inner surface of the membranes with a surfactant (HTBA). These cells have been shown to keep their liquid contents for at least two days without additional sealing.

Reference spectra in total electron yield technique have been recorded at the BL7-XPD chamber using dry powders fixed on indium foil.

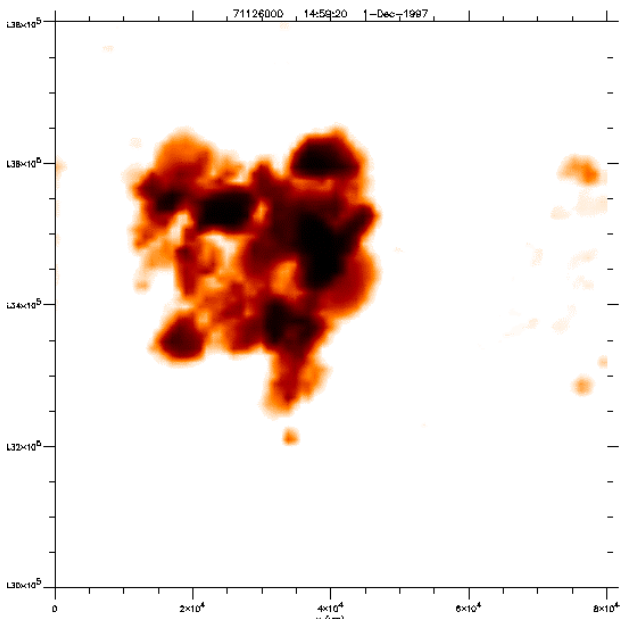

Fig. 1: Scanning X-ray micrograph (20µmx20µm) of Mn micro nodules.

RESULTS

Fig.1 shows a 20µm×20µm image taken at the BL7-STXM scanning transmission x-ray microscope with a spatial resolution of about 0.25µm. As generally observed for these samples, the micro nodules tend to form larger agglomerates which occur in a wide range of sizes and shapes. In the left part of Fig. 2 the Mn $L_{II,III}$ x-ray absorption spectra recorded at two different positions in such an agglomerate of nodules of sample 'orange' are compared. Additionally, reference spectra taken from aqueous solutions of Mn compounds (0.1M *KMn(VII)O_4* resp. 0.2M

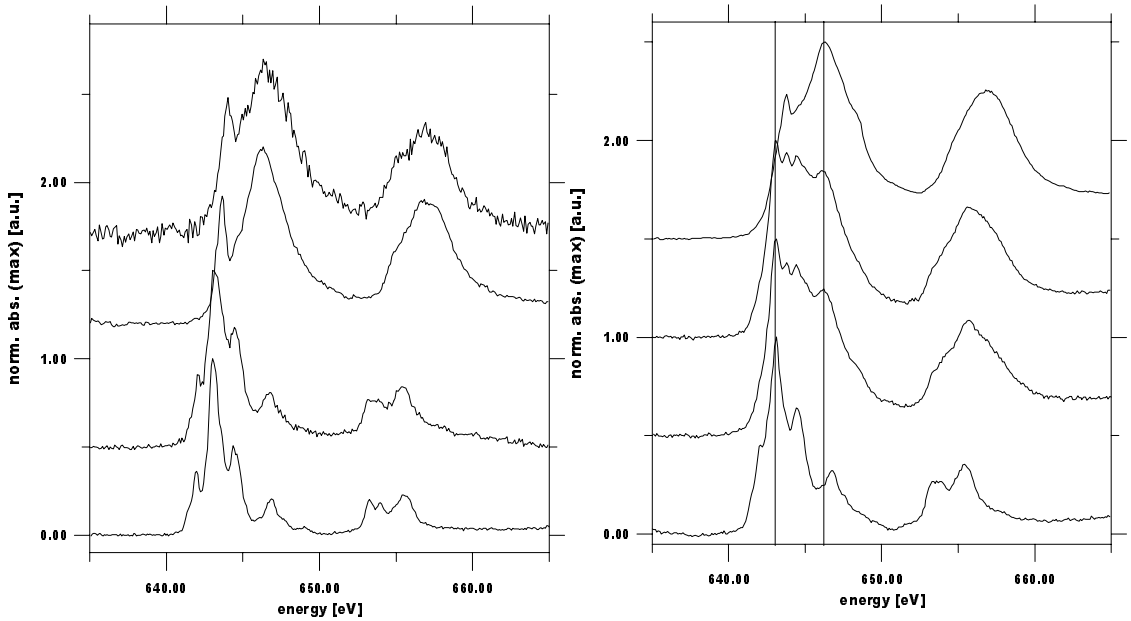

Fig. 2: Mn $L_{II,III}$ x-ray absorption measurements - left (from top to bottom): Mn micro nodules 'orange' (Pos. A), *KMn(VII)O_4*, Mn micro nodules 'orange' (Pos. B), *Mn(II)SO_4* - right (from top to bottom): *KMn(VII)O_4*, Mn micro nodule 'blue', Mn micro nodules 'orange', *Mn(II)SO_4* (all spectra have been normalized to their maximum intensity).

Mn(II)SO_4 in aq. dest.) are shown. The two lower spectra clearly exhibit the signature of a divalent Mn species, whereas the upper curve, in comparison to the reference compound *$KMnO_4$*, has to be ascribed to a valence state as high as +7. Considering the transmission measurements at a multitude of different sample spots, the +2 signature was by far the dominant characteristic of both samples—in fact it was the only one observed by STXM measurements for sample ‘blue’.

In the right part of Fig. 2 the corresponding Mn $L_{II,III}$ x-ray absorption spectra taken in total electron yield technique are compared. These spatially averaging measurements of the two different samples of Mn nodules turned out to expose a fine structure, which can be immediately explained as the superposition of the +2 and the +7 Mn spectral features. In contrast to the wet-cell transmission measurements, the total yield spectrum of sample 'blue' shows the contribution of the higher valence state. This can be from two causes. One is that the bulk of the particle is a +2 valence, with a ‘shell’ of higher oxidation state. The other is that sample preparation (drying in air) for the total yield measurement led to some additional oxidation. This ambiguity will be resolved in future experiments.

CONCLUSIONS

Soft x-ray absorption measurements of Mn micro nodules produced by bacterial biomineralization have been performed, both in the naturally hydrated and in the dry state. For the first time it has been shown that the high spatial resolution of the x-ray transmission

microscope STXM allows to differentiate between two species of the transition metal ions which are not homogeneously distributed throughout the agglomerates of micro particles. This can be seen as an important step towards the desired understanding of localized chemical processes induced by single cell microorganisms.

REFERENCES

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